Supporting Information
Polymerized Surface Micelles Formed under Mild Conditions

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1 Synthesis and characterization of LUPB

Lipoic acid anhydride: A mixture of lipoic acid (0.5 g, 2.5 mmol□ ACROS, 98□ purity) and dicyclohexylcarbodiimide (DCC, 0.33 g, 1.5 mmol, SCR, 95□ purity) was stirred in 15 mL of dry methylene chloride for about 10 h at room temperature under argon atmosphere. The product mixture was filtered to remove the byproduct. This solution was used directly in the synthesis of LUPB below.

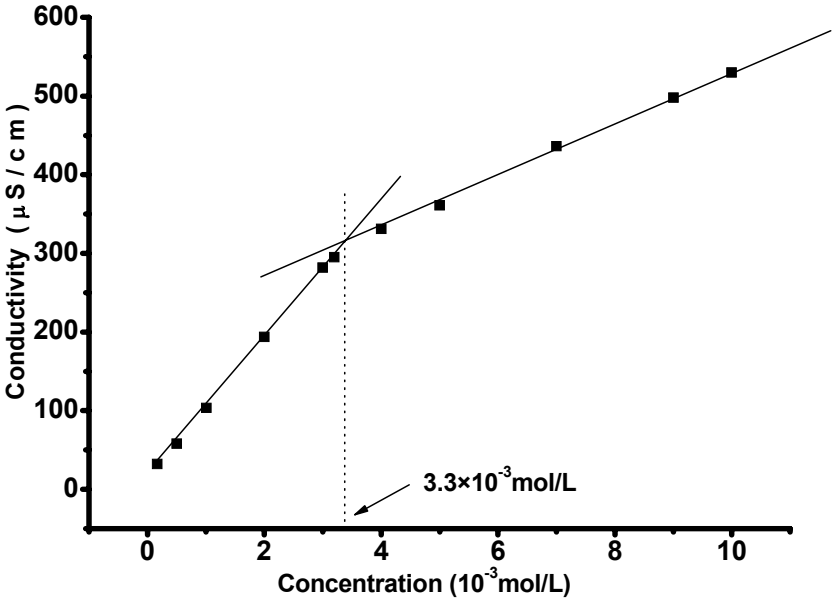
Lipoic acid (11-bromo undecyl) ester: 11-Bromo-1-undecanol (0.5 g, 2.0 mmol, Fluka, 99□ purity) was added to solution of lipoic acid anhydride containing 4-(dimethylamino) pyridine (DMAP, 0.30 g, 2.0 mmol, Fluka, 99□ purity) . After the mixture was stirred for 24 h under argon atmosphere at room temperature, thin-layer chromatography (SiO_2, CH_2Cl_2) indicated complete conversion to lipoic acid (11-bromo undecyl) ester. The product mixture then filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2), afforded 0.414 g (yield 45.3□). ^{1}H NMR (300MHz, $CDCl_3$, 25□, ppm): 4.13~4.00 (t, COO$\underline{CH_2}$, 2H), 3.63-3.50 (m, SS$\underline{CH}$, 1H), 3.45~3.35 (t, $\underline{CH_2}$Br, 2H), 3.24~3.05 (m, $\underline{CH_2}$SS, 2H), 2.37~2.26 (t, $\underline{CH_2}$COO, 2H), 2.44~2.22 (t, OCO$\underline{CH_2}$, 2H), 2.10~1.21 (m, $\underline{CH_2}$, 22H), 2.50~2.36, 1.95~1.81(m, m, SSCH$_2\underline{CH_2}$, 2H).

1-[11-(Lipoyloxy)-undecyl]-pyridinium bromide: Lipoic acid (11-bromo undecyl) ester (0.414 g, 0.9 mmol) was added to dry pyridine (15 ml). The mixture was stirred for 24 h under argon atmosphere at room temperature. Then the mixture was concentrated under reduced pressure to remove the unreacted pyridine. The product was dissolved in a minimum volume of solvent (CH_2Cl_2 : CH_3OH=3:1), and then recrystallized from ethylacetate, afforded 0.421 g (yield 86.5□). ^{1}H NMR (300MHz, $CDCl_3$, 25□, TMS, ppm): 9.58~9.46 (d, Py-$\underline{H}$, 2H), 8.56~8.45 (t, Py-$\underline{H}$, 1H) 8.19~8.05 (t, Py-$\underline{H}$, 2H), 5.05~4.92 (t, Py-$\underline{CH_2}$, 2H), 4.07~3.96 (t, $\underline{CH_2}$OOC, 2H), 3.60~3.40 (m, $\underline{CH}$SS, 1H), 3.21~3.02 (m, $\underline{CH_2}$SS, 2H), 2.34~ 2.21 (t, OCO$\underline{CH_2}$, 2H), 2.06~1.95 (m, Py-CH$_2\underline{CH_2}$, 2H), 2.50~2.36, 1.95~1.81(m, m, SSCH$_2\underline{CH_2}$, 2H), 1.73~1.10 (m, $\underline{CH_2}$, 22H). ^{13}C NMR (ppm): 173.25, 144.78, 128.07, 64.11, 61.72, 56.02, 38.14, 34.22,

33.76, 29.02, 28.99, 28.79, 28.66, 28.39, 28.22, 25.68, 25.52, and 24.36. ESI MS M^+ m/z Calcd. for $C_{24}H_{40}NO_2S_2^+$:438.71. Found: 438.42

2 The critical micelle concentration of LUPB

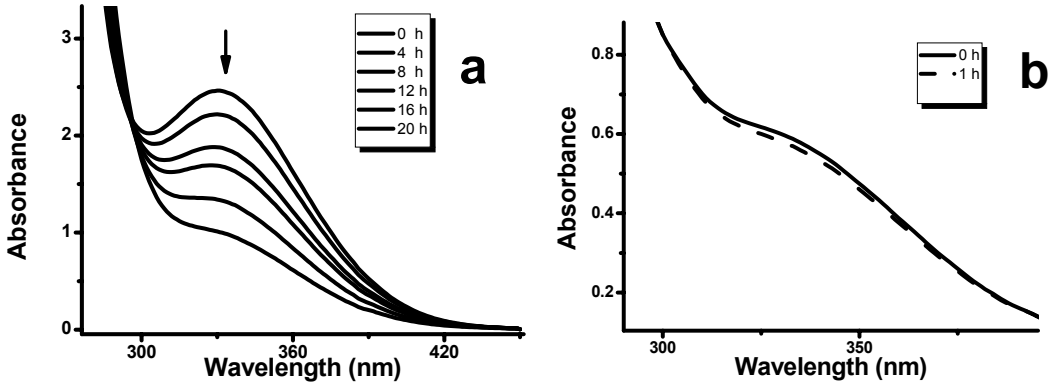
The critical micelle concentration (CMC) of LUPB was measured by concentration dependent conductivity. From the plot shown below we found that its CMC is 3.3×10^{-3} M.



S1 Dependence of the solution conductivity of LUPB on concentration, the CMC is 3.3×10^{-3} M.

3 Micelle polymerization

The ring-opening polymerization in the micelles was followed by UV-Vis spectroscopy (HITACHI U-3010 spectrophotometer). Typically, 3.4 mg (6.6×10^{-6} M) of LUPB was dissolved in 1 ml of 1×10^{-3} M HCl (pH 3) aqueous solution. Then its polymerization under such acidic condition was followed by UV-Vis spectroscopy, as shown in S2-a. The basic condition of pH 10 was adjusted by 1×10^{-4} M NaOH. Because of the process of polymerization under pH 10 was too fast to follow, the UV-Vis spectra we got was indicated the termination of the polymerization. The polymerization of LUPB with different concentrations was carried out in the same way.



S2. UV-Vis spectral changes accompanying the polymerization in micelles of surfactant LUPB under pH of (a) 3 and (b) 10, as a function of time.

4 Characterization of micelles and polymerized micelles at the interface by in situ atomic force microscopy (in situ AFM)

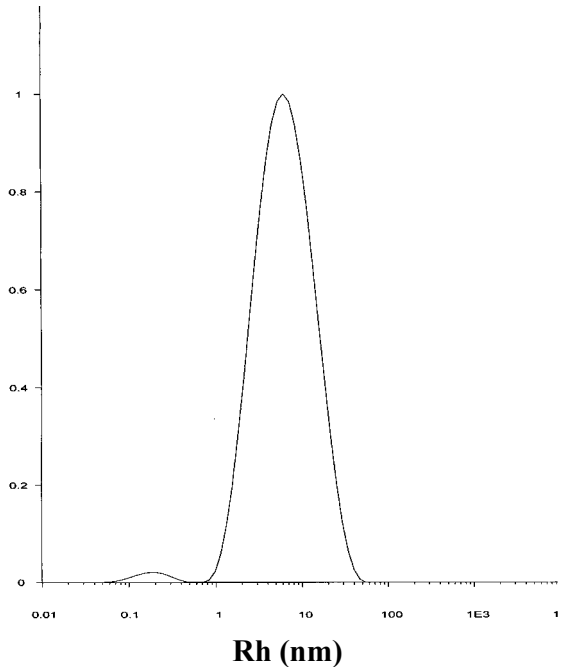
The surface micelles refer to micelles that are adsorbed onto solid substrates. In situ AFM images were captured by using commercial multimode Nanoscope IV (Digital Instrument, CA) with tapping mode in fluid at room temperature. The substrates used in the AFM studies were commercial mica and the mica was freshly cleaved before every time use.

Characterization of micelles: With the purpose to investigate the morphology of unpolymerized micelles adsorbed at the liquid/mica interface, 3.4 mg (6.6×10^{-6} M) of LUPB was dispersed in 1 ml of 1×10^{-3} M HCl aqueous (2 CMC) at room temperature. The solution was injected into the liquid cell and allowed for equilibrium at least 30 min before in situ AFM observation. Similarly, solution with concentration of 3.5×10^{-4} (≈0.12 CMC) below the CMC was prepared by dispersing 2.0 mg of LUPB in 10 ml of 1×10^{-3} M HCl aqueous solution.

Characterization of polymerized micelles: The polymerization of the micelles was carried out by dispersing 3.4 mg (6.6×10^{-6} M) of LUPB in 1 ml deionized water (≈2 CMC) at room temperature for 1 h. The termination of the polymerization was confirmed by UV-Vis spectroscopy. The solution of polymerized LUPB with concentration of 3.3×10^{-4} M below the CMC was obtained by diluting the polymerized micelles 20 times with deionized water. Before injected into the cell, the diluted solution was left for 2 h for incubation. Then in situ AFM was used to observe the adsorbed morphology at the liquid/mica interface.

5 Dynamic light scattering (DLS) study on micelles in solution

DLS indicates that the micellar aggregates of LUPB have an average hydrodynamic radius (Rh) of 6.2 nm measured at the concentration of 6.6×10^{-3} M at 25 □, as shown in S3. The DLS measurement is performed by ALV/DLS/SLS-5022F laser light scattering measurement system. Therefore the in situ AFM observation is well complemented by DLS.



S3. Hydrodynamic radius (Rh) distribution of the aggregates formed by LUPB at 25 □.